

Exhibit 50

Genesis of hexavalent chromium from natural sources in soil and groundwater

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Naturally occurring Cr(VI) has recently been reported in ground and surface waters. Rock strata rich in Cr(III)-bearing minerals, in particular chromite, are universally found in these areas that occur near convergent plate margins. Here we report experiments demonstrating accelerated dissolution of chromite and subsequent oxidation of Cr(III) to aqueous Cr(VI) in the presence of birnessite, a common manganese mineral, explaining the generation of Cr(VI) by a Cr(III)-bearing mineral considered geochemically inert. Our results demonstrate that Cr(III) within ultramafic- and serpentinite-derived soils/sediments can be oxidized and dissolved through natural processes, leading to hazardous levels of aqueous Cr(VI) in surface and groundwater.

manganese oxide | oxidation | serpentine | ultramafic | chromite | lophiolites

Hexavalent chromium is a toxin typically originating from anthropogenic activity (1). However, naturally occurring aqueous Cr(VI) at concentrations up to 73 µg liter⁻¹ have been reported in ground and surface waters from New Caledonia, California, Italy, and Mexico (2–7), values exceeding the World Health Organization's limit for drinking water of 50 µg of Cr(VI) per liter, or 960 nM Cr(VI). Processes for Cr(III) release to solution from chromite, the primary geological source for chromium, are perplexing because this mineral is known to be resistant to weathering, diagenesis, and low-grade metamorphic reactions (8). Manganese minerals that pervasively form as surface coatings on soil minerals and along fractures within Cr-rich rock strata may serve as potential oxidants of Cr(III). Here we illustrate that Cr(III) within chromite is oxidized when in association with the common Mn mineral birnessite, rectifying the generation of Cr(VI) from a Cr(III)-bearing mineral considered geochemically inert and explaining recent reports of naturally occurring Cr(VI) in groundwater (2–7) and chromium accumulation within plants (9, 10).

In the Earth's crust, chromium is concentrated (>200 mg kg⁻¹) in ultramafic rocks and serpentinites of ophiolite complexes that constitute ≈1% of the terrestrial landscape, primarily within populated areas of the Circum-Pacific and Mediterranean regions (Fig. 1). Chromium(III) concentrations in resulting soils and sediments are magnified by weathering and diagenetic reactions, where total Cr values ranging between 1,000 and 60,000 mg kg⁻¹ are common as a consequence of selective alteration of silicate minerals relative to chromite (2). Chromium(III) released during weathering readily adsorbs on clay minerals and precipitates as homogeneous solids or with Al(III)/Fe(III)-hydroxides (1). Despite the dominance of Cr(III)-species, recent discoveries of aqueous Cr(VI), a mutagen, teratogen, and carcinogen (11), in regions far afield from anthropogenic sources include the following: (i) spring waters from ultramafic rocks near Cazadero, in the coast ranges of California, where Cr(VI) concentrations are between 12 and 22 µg liter⁻¹ (2); (ii) pore-waters of serpentine soils in Tehama County, CA, having concentrations of 20 µg liter⁻¹ or greater (3); (iii) groundwaters from the ophiolite complex in the La Spezia Province of Italy exhibiting Cr(VI) concentrations between 5 and 73 µg liter⁻¹ (7); (iv) groundwater at León Valley,

Mexico, having Cr(VI) concentrations of 12 µg liter⁻¹ attributed to ultramafic rocks of the Sierra de Guanajuato (4); (v) groundwater from mafic alluvial deposits in the Mojave Desert having Cr(VI) concentrations of 60 µg liter⁻¹ (6); (vi) groundwater from the Aromas Red Sands aquifer in Santa Cruz County, CA, residing within an ophiolite complex having dissolved Cr(VI) concentrations ranging from 4 to 33 µg liter⁻¹ (12); and (vii) phosphorus-amended soils derived from ultramafic rocks in New Caledonia having pore-water concentrations of 700 µg liter⁻¹ (5). The New Caledonia soils have the highest reported Cr(VI) concentration, owing to the presumptive displacement of Cr(VI) from mineral surfaces by phosphate, which has been added to the soil as a nutrient amendment (5).

Although chromite [FeCr(III)₂O₄] is the primary source of Cr in ultramafic and serpentinite rocks (13), it exhibits very low solubility under most geologic and industrial refining conditions (14–16), and there are few naturally occurring oxidants of Cr(III). The only natural oxidants of aqueous Cr(III) at pH < 9 are Mn(IV/III)-oxides (17–21) and hydrogen peroxide (H₂O₂) (22). Reactions between chromite and Mn-oxide minerals, producing Cr(VI) in subsurface aqueous environments, have been suspected (1, 7, 9, 23) but remained unresolved. To evaluate processes by which Cr(III) may be dissolved from ultramafic or serpentinite rocks, and related soils and sediments, and subsequently oxidized to form aqueous Cr(VI), we investigated the time-dependent oxidation/dissolution of chromite by the Mn mineral birnessite. Birnessite is a mixed-valence Mn(IV/III)-oxide mineral having a layered structure that commonly forms surface coatings on weathered mineral grains in ultramafic rocks and serpentinites; the form used here had a formula of K_{0.16}Mn^{III}_{0.16}Mn^{IV}_{0.84}O₂. In addition, we further examined Cr(III) oxidation by birnessite in soils derived from serpentinites.

Results

Rates of Cr(III) release from chromite and oxidation upon reaction with birnessite were experimentally determined at ambient conditions as a function of pH and mineral suspension densities (see *Materials and Methods* and Table 1). Relative proportions of chromite and birnessite suspension densities for these experiments were based on concentrations of Cr and Mn in serpentine soils (8) and measured surface areas of chromite (0.25 m² g⁻¹) and birnessite (125 m² g⁻¹; see *Materials and Methods*). Oxidative dissolution of chromite in the presence of birnessite produces aqueous Cr(VI) on the timescale of hours, with formation rates ranging from 0.5 to 4.1 nM h⁻¹ (Fig. 2). Chromium(III) released by dissolution of chromite in the absence of birnessite in our experiments over a period of 450 h is below the detection limits of 85 nM, confirming the common resistance of chromite in weathering and diagenetic environments.

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The authors declare no conflict of interest.

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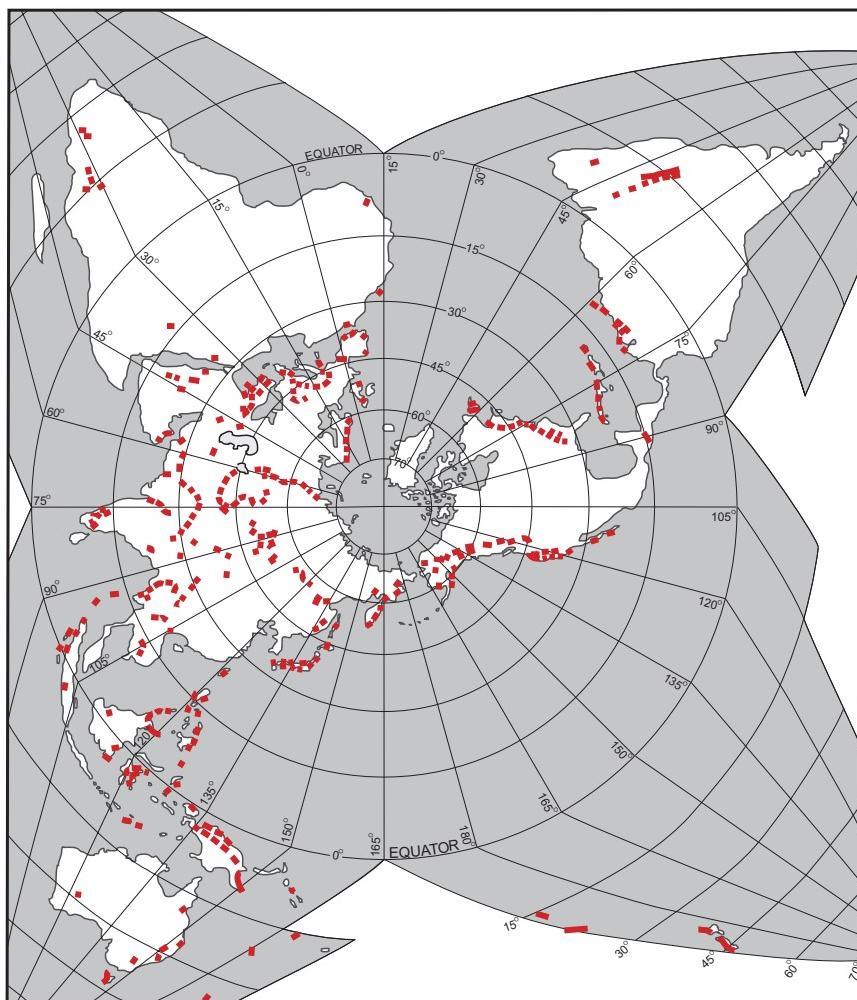


Fig. 1. A north polar projection showing the distribution of serpentinites and ophiolites (red) (data from R. G. Coleman, personal communication).

ments (8). Aqueous Mn concentrations were near or below detection limits ($<0.1 \mu\text{M}$) for the duration of all of the experiments. Aqueous iron concentrations initially increased to $\approx 0.5 \mu\text{M}$ and then decreased rapidly to a relatively constant

concentration of $0.2 \mu\text{M}$ as a likely consequence of Fe(II) oxidation and subsequent Fe(OH)_3 precipitation; acidic dissolution (0.5 M HCl) of the products demonstrates minimal Cr (<5% wt) associated with the secondary phases.

Table 1. Reaction parameters used for chromite and birnessite experiments

Experiment	Chromite,* g	Birnessite, [†] g	pH [‡]	Suspension density, [§] $\text{m}^2 \text{liter}^{-1}$	
				Chromite	Birnessite
A	0.8	0.43	5	0.2	54
B	0.8	0.86	5	0.2	108
C	0.8	2.0	5	0.2	250
D	0.3	0.86	5	0.08	108
E	0.08	0.86	5	0.02	108
F	0.04	0.86	5	0.01	108
G	0.3	0.86	3	0.08	108
H	0.3	0.86	6.7	0.08	108
I	0.3	0.86	8	0.08	108
Chromite	0.8	—	5	0.2	—
Birnessite	—	0.43	5	—	54

*Chromite chemical composition is $(\text{Fe}_{0.46}\text{Mg}_{0.52}\text{Mn}_{0.02})(\text{Cr}_{0.61}\text{Al}_{0.29}\text{Fe}_{0.10})_2\text{O}_4$.

[†]Synthetic birnessite.

[‡]10 mM acetate buffered solution (pH 5), HCl buffered (pH 3), 5 mM MES buffer (pH 6.7), and NaOH buffer (pH 8).

[§]Measured BET analyses: Chromite surface area is $0.25 \text{ m}^2 \text{ g}^{-1}$, and birnessite surface area is $125 \text{ m}^2 \text{ liter}^{-1}$.

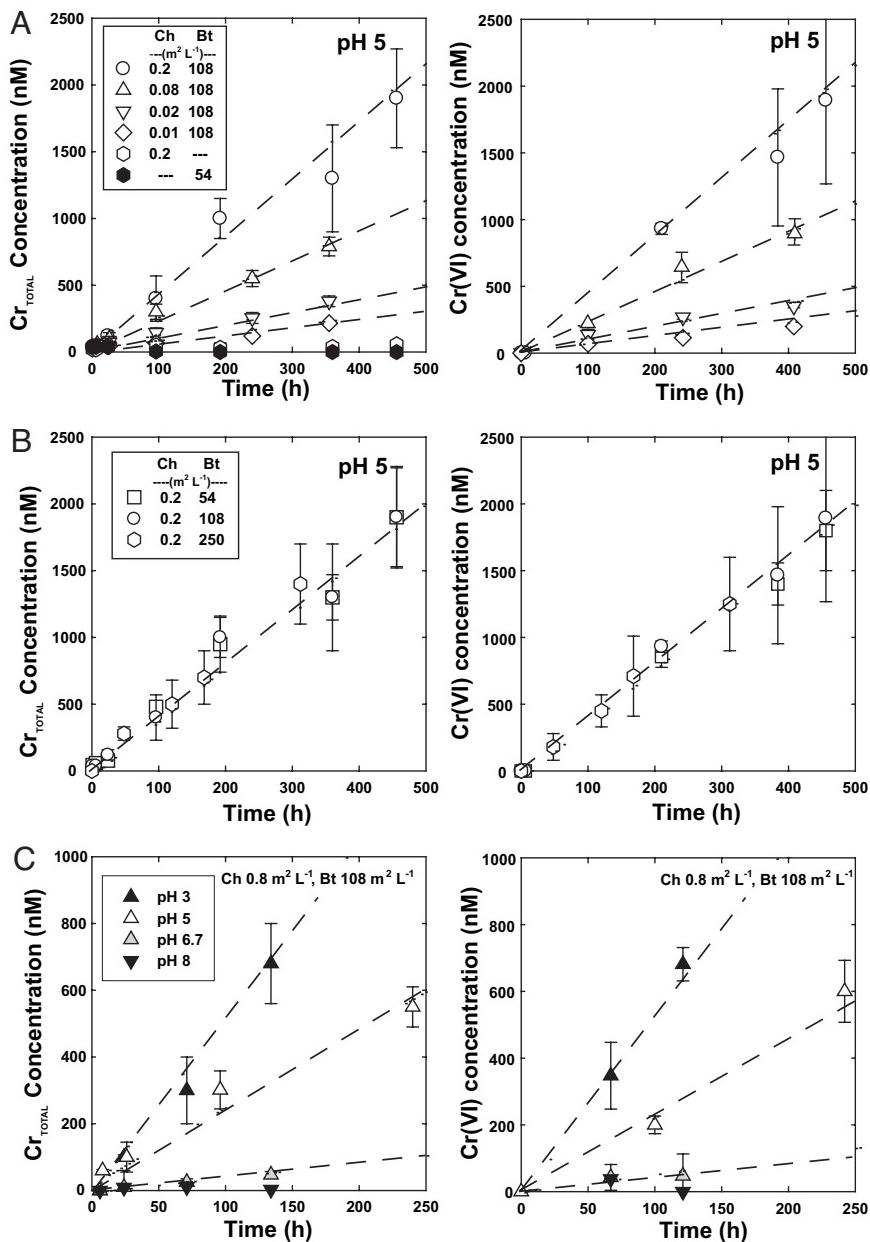


Fig. 2. Concentration of total aqueous Cr and Cr(VI) as a function of time for experiments evaluating variable chromite (Ch) suspension densities at pH 5 (A), variable birnessite (Bt) suspension densities at pH 5 (B), and constant chromite and birnessite suspension densities and variable pH (C). Data, which are the average of triplicate samples (error bars represent the standard deviation of replicates), are fit by linear regression (dashed lines).

Our experimental rate for aqueous Cr(VI) formation has a near-linear dependence (reaction order of 0.7) on chromite suspension density, whereas the pH dependence is nonlinear and well described by using a polynomial function (Fig. 3C) under the conditions evaluated here. In contrast, the rate of Cr(VI) formation at pH 5 is independent of the amount of birnessite at suspension densities $>54 \text{ m}^2 \text{ liter}^{-1}$, yielding a consistent Cr(VI) formation rate of 4.1 nM h^{-1} (Figs. 2B and 3B). Suspensions of chromite and birnessite produce Cr(VI) at a rate that can be described by

$$d[\text{Cr(VI)}]/dt = k' \{\text{Chromite}\}^{0.7}, \quad [1]$$

where k' is $(1.6pH^2 - 25pH + 97) \text{ nM liter}^{0.7} \text{ m}^{-1.4} \text{ h}^{-1}$, $\{\text{Chromite}\}$ is the chromite suspension density in $\text{m}^2 \text{ liter}^{-1}$,

birnessite suspension densities are $>54 \text{ m}^2 \text{ liter}^{-1}$, and pH values are between 3 and 8.

The sparing solubility of chromite and birnessite might be expected to limit the reaction between Cr(III) and Mn(IV/III), and indeed the rates of Cr(VI) formation by reaction of aqueous Cr(III) with Mn oxides minerals, including birnessite (17–21), are all much faster ($\gg 10 \text{ nM h}^{-1}$) than those observed in our experiments where the source of Cr(III) is chromite. Nevertheless, our experiments demonstrate that chromite and birnessite readily react in suspension to yield aqueous Cr(VI) despite their limited solubilities. A fractional-order dependence on chromite and independence on birnessite suspension densities (Fig. 3B) suggests that the reaction pathway involves Cr(III) dissolution from chromite and transport of aqueous Cr(III) to the birnessite surface. The larger production rate of aqueous Cr(VI) with

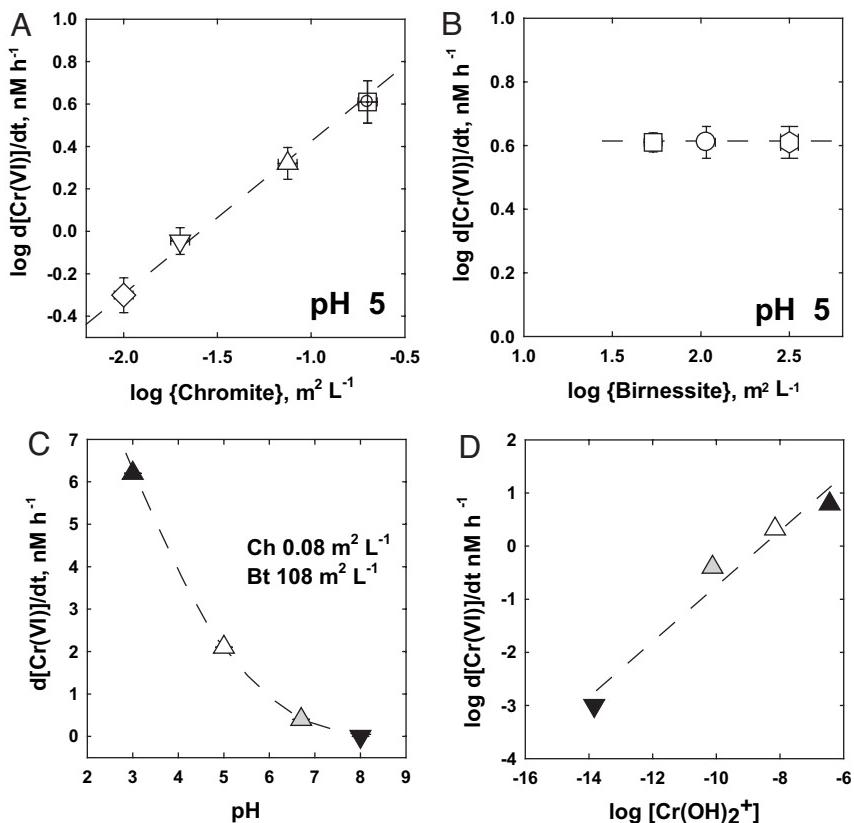


Fig. 3. Rates of aqueous Cr(VI) produced as a function of chromite (Ch) suspension density (A), birnessite (Bt) suspension density (B), pH (C), and Cr(OH)₂⁺ concentrations (D) (predicted from the calculated solubility of chromite). Within each plot, the best fit for these data are shown yielding the descriptive equations $\log d[Cr(VI)]/dt = 0.7\log\{Chromite\} + 1.1$ (A); $\log d[Cr(VI)]/dt = 0.61$ (B); $d[Cr(VI)]/dt = 0.26pH^2 - 4.1pH + 16$ (C); and $\log d[Cr(VI)]/dt = 0.5[Cr(OH)_2^+] + 4.5$ (D). The symbols in A correspond to those in Fig. 2 A and B; symbols in C and D correspond to those in Fig. 2C.

decreasing pH (Fig. 2C) is consistent with the solubility of chromite (and birnessite) being inversely related to pH (15). Furthermore, as shown in Fig. 3D, our experimental rate of aqueous Cr(VI) production is proportional to the dissolved concentration of Cr(III) predicted from the estimated solubility of chromite (15), exhibiting a log-linear dependence relative to the calculated concentration of the Cr(OH)₂⁺ aqueous species; hydrolysis products of aqueous Cr(III), and hydrolyzable metals in general, have increased reactivity owing to accelerated water exchange rates (24). Upon adsorbing to birnessite, Cr(III) is oxidized through a multistep process to Cr(VI), where the successor complex of H_xCrO₄^{x-2}²⁻ is then released to the aqueous solution (25). The rates observed here for the reaction of chromite and birnessite suggest that Cr(VI) can be generated within soils and sediments through the reaction of solids with limited solubility on timescales rapid enough to provide measurable concentrations of Cr(VI) in groundwater and soil porewater. To further test this premise and the validity of the developed rate expression, we measured the rate of Cr(VI) formation within serpentinite-derived soils.

We measured production of aqueous Cr(VI) within three serpentinite soils, two Mollisols from Jasper Ridge, CA, and an Oxisol from New Caledonia, with and without the addition of birnessite, and we conducted a comparative analysis to evaluate our rate expression for chromite reacting with birnessite (Table 2). Chromite suspension densities were estimated for the soils by assuming that analyzed Cr concentrations are due to spherical grains of chromite present within the sand-sized fraction (2, 8). For calculating reaction rates, we further assumed that birnessite is present within the soil at a suspension density sufficient to

yield a zero-order rate dependence. The experimental rates of dissolved Cr(VI) formation in New Caledonia soil, a mature soil having Cr(III) within chromite and minor Cr(III)-Fe(III) (hydr)oxides (2), are 0.9 nM h⁻¹ without and 1.3 nM h⁻¹ with birnessite addition, both in close agreement with our predicted Cr(VI) formation rate of 1.3 nM h⁻¹ (Table 2). Rates of Cr(VI) production measured in solution for both Jasper Ridge soils are 1.3 nM h⁻¹, and despite our assumption of being independent of birnessite concentration, rates increased to 4.4 nM h⁻¹ with its addition. Our rate expression, with the simplifying assumptions noted above, overpredicts the rate of Cr(VI) formation in unamended soils from California (by factors of ≈1.3–1.5) and underpredicts them upon addition of birnessite (by a factor of ≈0.4; Table 2). Accelerated Cr(VI) production upon addition of birnessite in the upland Mollisols is consistent with a mineralogy dominated by clays and limited development of metal oxides such as birnessite. Trace quantities of Cr-bearing chlorite in the California soils, noted by electron microprobe analysis (8), would lead to a Cr(VI) production rate more rapid than predicted based on our rate expression for chromite alone.

Discussion

Aqueous concentrations of Cr(VI) in soils and sediments derived from ultramafic or serpentinite rocks are dependent on the mass balance between average rates of production and consumption; the latter is largely due to direct (enzymatic) or indirect (metabolite) reduction of Cr(VI) to Cr(III) by microorganism, and to sorption of Cr(VI) onto Fe(III) and Al(III) (hydr)oxides. Rates of aqueous Cr(VI) production are primarily controlled by the solubility and dissolution rates of Cr(III) host minerals, the

Table 2. Serpentine soil (10 g) and birnessite batch experiments in 0.1 liter of solution

Samples	Birnessite mass, g	Total Cr _{soil} ,* mg kg ⁻¹	Chromite mass in soil sample, [†] g	Estimated chromite suspension density, [‡] m ² liter ⁻¹	Measured Cr(VI) rate, nM h ⁻¹	Calculated Cr(VI) rate, [§] nM h ⁻¹
Jasper Ridge						
JR1	—	5,976	0.13	0.08	1.3	2.0
JR1 w/birnessite	0.1	5,976	0.13	0.08	4.4	2.0
JR2	—	4,978	0.11	0.06	1.3	1.7
JR2 w/birnessite	0.1	4,978	0.11	0.06	4.4	1.7
New Caledonia						
NC	—	827	0.015	0.04	0.9	1.3
NC w/birnessite	0.1	827	0.015	0.04	1.3	1.3

Solution: mM acetate buffer (pH = 5).

*Total Cr concentrations were obtained through total digestion and ICP-OES analyses.

[†]Chromite mass in the sample is based on observations made by Oze *et al.* (2, 8) and assuming total Cr_{soil} is representative of only chromite.[‡]Estimated chromite suspension densities are calculated based on (*i*) observations that chromite grains in these soils are dominantly in the sand-sized fraction (2, 8), (*ii*) treating each chromite grain as a sphere, (*iii*) using a chromite density of 3 g cm⁻³, and (*iv*) a chromite formula weight of 223.8 g mol⁻¹.[§]Calculated using the assumptions above and the rate equation discussed in the text.

solution pH, and the accessibility of aqueous Cr(III) to mixed valence Mn(IV/III)-oxides that coat mineral surfaces and pore spaces in sediments and soils of ultramafic and related rocks. The presence of Cr(III)-silicates, including diagenetic and low-grade metamorphic layer silicates (2, 8), will lead to the fastest rates of Cr(VI) production, and pH influences on Cr(VI) production will differ. For example, we predict limited Cr(VI) production from chromite in serpentinites where formation waters are highly alkaline (1), but significant formation of Cr(VI) in serpentine soils where pH values (2) are often <7 (Fig. 3C); Cr-silicate mineral dissolution, in comparison, would be appreciable under highly alkaline conditions and lead to higher rates of Cr(VI) generation.

Considering chromite as a conservative phase of Cr(III), our experiments reveal that even at circumneutral pH, Cr(VI) formation rates of 4.1 nM h⁻¹ can lead to aqueous Cr(VI) concentrations exceeding World Health Organization standards of 50 µg liter⁻¹ within 100 days; within soils/sediments at pH 5, pore-water residence time of <10 days could lead to concentrations >50 µg liter⁻¹. Countering production, however, will be Cr(VI) reduction, a process transpiring through biologically mediated and abiotic pathways and dominating the fate of Cr under anaerobic conditions (26–29). Reduction within aerobic soils/sediments will be linked primarily to microbial oxidation of organic matter. Generation of Cr(VI) through oxidation of native sources of Cr(III) such as chromite would be most prolific in soils/sediments with limited organic matter and under acidic conditions. Considering the broad distribution of ultramafic and serpentinite rocks and related soils/sediments (Fig. 1), geologically derived Cr(VI) may be widely distributed within groundwaters; our results provide estimates of the potential for aqueous Cr(VI) production rates within such environments, which when coupled with reduction reactions allows predictions of Cr(VI) concentrations. Recent, and increasing, reports of Cr(VI) within groundwater and surface waters derived from contact with ultramafic material (2–7, 9, 10) demonstrate that the overall rate of aqueous Cr(VI) production locally exceeds its retention in solids or reduction to Cr(III) and illustrate the importance of geologic (natural) Cr described here.

Materials and Methods

Chromite used in the experiments was natural material obtained from Barnes Environmental, Inc. (Waterdown, ON,

Canada). A 160- to 250-µm-size fraction of chromite was prepared by cleaning in multiple ultrasonic isopropanol baths and rinsed several times in distilled, deionized water and 0.01 M HCl; further impurities were removed by using a slope Franz magnetic separator. After optical examination, chromite was crushed into a powder and rinsed several times in distilled, deionized water and 0.01 M HCl. The average composition of the chromite, on the basis of 25 electron microprobe analyses, was (Fe_{0.46}Mg_{0.52}Mn_{0.02})(Cr_{0.61}Al_{0.29}Fe_{0.10})₂O₄, and it had a surface area of 0.25 m² g⁻¹, as determined by using N_{2(g)} and Brunauer–Emmett–Teller (BET) isotherm. Birnessite was synthesized by using the procedure described by Buser *et al.* (30) and modified by Fendorf and Zasoski (20). The mineralogy of the synthetic birnessite was confirmed by using x-ray diffraction (XRD) and had a surface area of 125 m² g⁻¹ based on BET analyses.

A series of batch experiments were performed in triplicate by using 1-liter polypropylene bottles at ≈25°C and a range of chromite and birnessite suspension densities (Table 1). After weighing and loading chromite and birnessite, 1 liter of (*i*) hydrochloric acid (HCl) buffered solution (pH 3), (*ii*) 10 mM acetic (CH₃COOH) solution at pH 5, (*iii*) 10 mM (morpholino)-ethanesulfonic acid (MES) solution at pH 6.7, or (*iv*) sodium hydroxide (NaOH) buffered solution at pH 8 was added. The pH values of all buffered solutions and Eh (≈400 mV) were constant with respect to time. Chromite and birnessite were also run individually in the 10 mM acetic acid solution. Solutions were shaken gently every 6 h to prevent particle grinding. Aliquots were extracted from the polypropylene bottles by using a syringe and passed through a 0.2-µm filter before analysis. Less than 40 ml was extracted over the course of each experiment resulting in a total volume change of <4%. Production of soluble Cr(VI) was measured spectrophotometrically at 540 nm using the *s*-diphenyl carbazide method modified from Bartlett and James (31). Soluble Fe(II) was monitored by using the ferrozine method adopted from Stookey (32). Total dissolved Cr, Fe, and Mn were measured by using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Soils derived from serpentinite bedrock collected from Jasper Ridge Biological Preserve (Stanford, CA) and New Caledonia were used to determine the influence of birnessite in soils known to contain chromite. Jasper Ridge serpentine soils contain Cr-bearing minerals including chromite, Cr-magnetite, and Cr-

chlorite; however, Cr enrichment is directly related to the abundance of chromite (8). A majority of the Cr related to New Caledonia serpentine soils is attributed to Cr (oxy)hydroxides; however, chromite constitutes an appreciable fraction of these soils as well (2). Birnessite was added (0.1 g) to the soil in a second set of experiments to test the impact of birnessite suspension density on the rate of Cr(VI) generation.

Ten grams of the <250 µm size-fraction of two soils from Jasper Ridge (JR1, JR2) and one from New Caledonia was added along with 100 ml of 1 mM acetic acid (pH 5) into 150-ml

Nalge bottles. Aqueous solutions were evaluated as a function of time. Additionally, 10 g of each soil, 0.1 g of birnessite, and 100 ml of 1 mM acetate-buffered solution (pH 5) were loaded into 150-ml Nalge bottles and were allowed to react. The reaction vessels were mixed by rotation at a rate of 2 revolutions per min. Solutions were removed with a syringe and passed through a 0.2-µm filter before analysis.

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